

**ELECTROCHEMICAL SYNTHESIS OF NANOSTRUCTURED TiO₂ THIN FILMS:
SURFACE CHARACTERIZATION**

DIANA CAROLINA ZAPATA DOMÍNGUEZ



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FACULTAD DE CIENCIAS NATURALES Y EXACTAS
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SANTIAGO DE CALI
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**FACULTAD DE CIENCIAS NATURALES Y EXACTAS
DEPARTAMENTO DE QUÍMICA**

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Por:

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1. LIST OF ABBREVIATIONS, ACRONYMS AND SYMBOLS

1D	one dimension
2D	two dimension
3D	three dimension
AC	alternating current
DC	direct current
E°	standard electrode potential
I	current density
kX	0.1 millimeter
EG	ethylene glycol
SEM	scanning electron microscopy
UV	ultraviolet
XRD	X-ray diffraction

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4. ABSTRACT

This work describes the electrochemical synthesis of nano-structured TiO₂ films on titanium substrates in mixed water-ethylene glycol solutions containing HF or NH₄F. The major electrolysis variables such as cell voltage, electrolyte composition, and synthesis time affect the morphology of the films. While films with irregular morphologies were attained in acidic media, films showing regular nanotubular structures were attained under neutral pH conditions. The length of the tubes, the tube diameter and other features heavily depend on the content of NH₄F in the electrolysis medium and the time of the reaction. The presence of water influences the formation of ribs around the tubes and of irregular deposits on the tubes mouth. Increasing the cell voltage decreases the thickness of the tube walls. If the electrolysis time is sufficiently large, the internal walls of the tube break open and the interior of the films exhibit a cave-like structure. XRD analysis shows that the films prepared at room temperature are amorphous but crystalline anatase and rutile structures develop upon annealing in the temperature range between 300 and 700 °C.

Keywords: Electrochemistry, anodizing, nanotubes, titanium dioxide.

5. INTRODUCTION

Nanoscience is loosely defined as the study of materials that have at least one dimension in the 10^{-7} to 10^{-9} m range. One can further classify nanomaterials as one dimension (1D, such as nanobelts, nanowires, nanorods, and nanotubes), two dimension (2D, such as nanosheets), and three dimension (3D, such as polycrystals). The main characteristic of nanosize materials is their large surface-to-volume which may significantly alter these materials reactivity and several physical and mechanical properties (for instance, magnetic characteristics, electronic conductivity, hydrophobicity, morphology and hardness) with respect to those of their bulk counterparts.

The electrochemistry group at Universidad del Valle is interested in nanomaterials of metal oxides, for example Al_2O_3 , ZnO and TiO_2 because these oxides can be used in catalysis, separations, gas storage and chemical sensors to name a few applications. In particular nanomaterials based on titanium dioxide are of interest because of this material relatively low toxicity to humans and the environment. Control of the morphology of TiO_2 nanoparticles and thin films can be achieved by chemical and electrochemical method, respectively. However, reproduction of the synthesis of published procedures is not straightforward. Consequently, the present research work is a systematic study on the synthesis variables (cell voltage, electrolyte composition, and synthesis time) that affect the morphology of TiO_2 thin films grown by electrochemical oxidation of titanium foils.

6. BACKGROUND AND THEORETICAL FRAMEWORK

Titanium dioxide nanomaterials can be made by hydrothermal methods, the sol-gel techniques, and anodic oxidation¹. The hydrothermal method is a top-down approach to prepare TiO₂ nanotubes from TiO₂ powder in aqueous solutions at moderate temperatures² (see Figure 1).

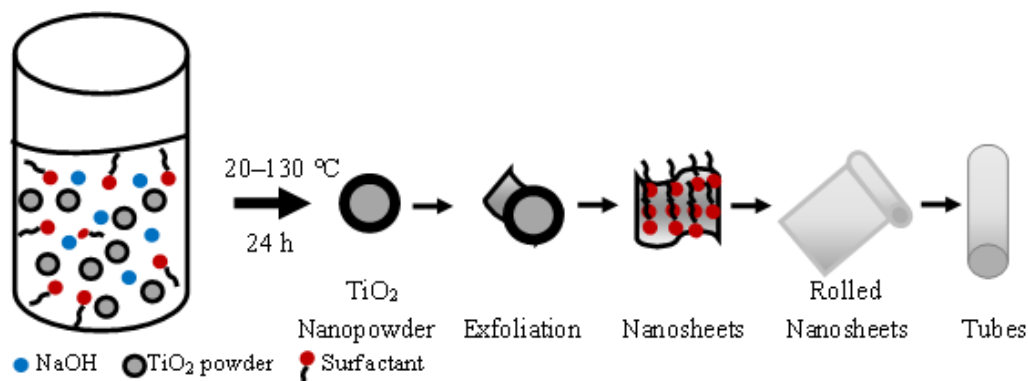


Figure 1. Hydrothermal synthesis of nanostructured.

The Sol-Gel technique is a bottom-up approach by which a sol or colloidal suspension is prepared by acid-catalyzed hydrolysis of titanium (IV) alkoxides. Then, the suspension is deposited on an anodic alumina membrane templates, which has a porous, tubular morphology. Then, the sol loses solvent and the TiO₂ material changes to gel or solid gel phase within the pores of the alumina template. Finally, removal of the alumina membrane renders TiO₂ nanotubes².

Both the hydrothermal and the sol-gel procedures yield TiO₂ agglomerates with a wide distribution of tube lengths and diameters. However, for several applications, a well-defined and regular morphology with low size distribution is necessary.

Another way to produce nanotubes of TiO₂ is by anodizing titanium in an electrolytic cell at high anodic potential. The cell is typically in a two-electrode configuration with an inert metal (such as Pt) as the cathode (see Figure 2). Electrochemical oxidation of titanium in a mixed aqueous-organic medium containing fluoride ions produces nanoscale smooth tubes of titanium dioxide. Electrolytic methods lead to specific and controllable orientation of nanotubes, in contrast with the two methods described above.

Figure 2 is a scheme of the growth of TiO_2 , first, as a compact oxide layer that is then etched by fluoride ions to form pores. Well-formed nanotubes grow under two competing factors, dissolution of titanium from electrode and formation of compact oxide layer. Adjustment of the experimental conditions leads to the formation of either pores or nanotubes³. It has been shown that the electrolyte composition, cell voltage and temperature are all important to control the morphology of the resulting films⁴.

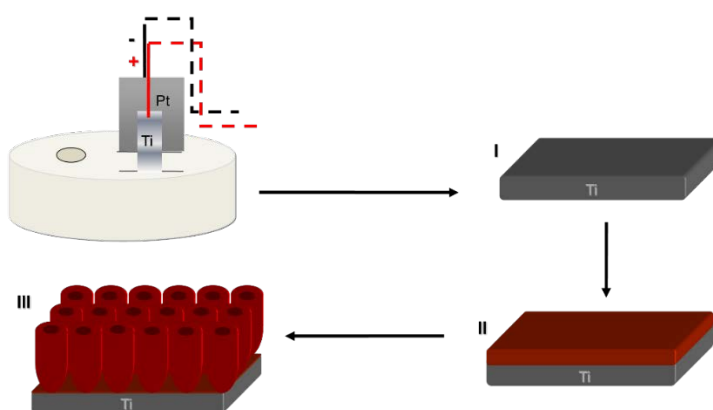


Figure 2. Scheme of the electrolysis cell and growth of TiO_2 .

In early experiments (so-called electrosynthesis of the first generation), the cell voltage is low (in the range from 5 to 20 V) and the electrolytic medium is aqueous, acidic, consisting of mixture HF with sulfuric, acetic, phosphoric or nitric acid^{5,6}. This first generation of conditions yields films with poor morphological control and short nanotube length and diameter. In a second generation of experiments, the electrolytic cell contains HF, NH_4F or KF in an aqueous, neutral medium^{7,8}. Although, morphology control is still poor because fast electrochemical etching and high hydrolysis rates of titanium occur simultaneously.

Application of higher cell voltages (up to 100 V) and switching of the electrolysis medium to a low aqueous + high organic mix (electrosynthesis of the third generation) improves nanotube morphology and reduces tube splitting. In this third generation electrosynthesis, the cell contains NH_4F and organic solvents, such as ethylene glycol^{9,10}, glycerol¹¹, formamide¹², and dimethyl sulfoxide¹³. It has been reported that a neutral medium with low water and high organic content, at the expense of higher cell voltage, leads to smooth tube walls.

The mechanism of nanotube growth is still a matter of debate. One of the proposed mechanism, the so-called field-assisted dissolution process, consists of the ejecting of Ti^{4+} from Ti foils and the incorporation of anions (F^- , O^{2-}) from the electrolyte to the oxide to ensure the formation of the pores at the metal-oxide or oxide-electrolyte interface. However, the field-assisted dissolution process cannot explain the large thickness of some TiO_2 nanotubes¹⁴.

In the dissolution process, solvent decomposition products and fluoride ions are incorporated at the metal-oxide interface. For example at high voltage, ethylene glycol produces soluble molecules such as glycolic acid that further decompose to CO_2 ^{15,16}.

7. PROBLEM

Titanium dioxide nanotubes have been electrochemically synthesized for the past 15 years. However, reproduction of experimental conditions reported in literature is not necessarily trivial because film morphology changes with many experimental variables, such as cell medium composition (aqueous or non-aqueous), electrolyte type and pH, cell type (one compartment or two compartment), temperature, mass transport mode (diffusion or convection), cathode materials, anode-cathode separation, anode geometry (flat vs tridimensional), electrolytic mode of operation (voltage or current control), and type of imposed electrochemical signal (DC or AC). The electrochemistry group at Universidad del Valle is interested in the electrosynthesis of TiO_2 nanotubes with tailored morphologies to be used in photo-assisted catalysis and as matrices for chemical sensors and biosensors.

This exploratory work is part of a joint-project with Thin-Film Research Group from the Physics Department. In this regard, this work shows the morphology variation of TiO_2 thin films as function of applied voltage and synthesis time in mixed water-ethylene glycol containing media with HF or NH_4F as electrolyte and etching agent.

8. OBJECTIVES

8.1 General goal:

To synthesize nanostructured thin film of titanium dioxide in an electrochemical cell under potentiostatic control.

8.2 Specific goals:

- To study changes of the morphology of the films through variations in cell voltage, electrolyte composition and synthesis time.
- To characterize the morphology and crystal structure of as grown samples of TiO_2 films by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

9. EXPERIMENTAL SECTION

Titanium anodes (0.5 cm x 1.0 cm) were made from titanium metal foil (Alfa Aesar, 99.6%, thickness=0.05 mm). Platinum cathodes (1.0 cm x 1.0 cm) were made from metal foil (Alfa Aesar, 99.9%, thickness=0.127 mm). Before electrolysis, both titanium and platinum electrodes were degreased in an ultrasonic bath (Branson 1510) in deionized water and acetone (Merck, ACS reagent) for 10 min each, followed by drying the samples in a nitrogen stream. Electrolysis experiments were performed in a Teflon, single-compartment, electrochemical cell (volume= 8 mL) with a DC power supply (MCP Lab Electronics M10-QS1003) under controlled cell voltage, electrolyte composition and synthesis time. Anode-cathode separation was kept constant at 1.0 cm.

Aqueous solutions were prepared with deionized water. HF (48% Merck), NH_4F (JT Baker) and ethylene glycol (JT Baker, analytic reagent containing 0.2% H_2O) were used as purchased. All the electrosynthesis experiments were carried out at room temperature (25–30 °C) in the electrochemistry laboratory in Cali.

9.1 Morphology of TiO_2 films prepared in acidic medium as a function of electrolysis time

The acidic electrolyte was prepared from mixture of 50% water + 50% ethylene glycol (0.2% v/v HF, pH 2.18). The electrochemical oxidation of Ti foils was conducted at 90 V constant voltage for 2, 5 and 10 hours (samples 1, 2 and 3, respectively).

9.2 Influence of fluoride concentration on TiO₂ films morphology

The electrolytic solutions were prepared from mixture of 5% water + 95% ethylene glycol (containing different NH₄F concentration, pH 6.0). The fluoride ion content was varied in the range from 0 to 0.500% (samples 4 to 10) as summarized in Table 1. The applied cell voltage was 70 V for 120 min.

Table 1. Experimental conditions for the study of the influence of fluoride ion content on TiO₂ films morphology.

Sample	Voltage (V)	H ₂ O (%)	EG (%)	NH ₄ F (%)	Time (min)
4	70	5	95	0.000	120
5				0.015	
6				0.045	
7				0.075	
8				0.150	
9				0.250	
10				0.500	

9.3 Influence of the water content on the morphology of TiO₂ films

The electrolytic solutions were prepared by varying the concentration of water and ethylene glycol while keeping the concentration of NH₄F at 0.250% w/v (pH 6.0). The experimental conditions are summarized in Table 2.

Table 2. Experimental conditions for the study of the effect of water content on TiO₂ films morphology.

Sample	Voltage (V)	H ₂ O (%)	EG (%)	NH ₄ F (%)	Time (min)
11	70	0	100	0.250	120
12		2	98		
13		4	96		
9		5	95		
14		6	94		
15		8	92		
16		10	90		

9.4 Effect of the cell voltage on TiO₂ film morphology

The electrolytic solutions contained 5% water + 95% ethylene glycol (with 0.25% w/v NH₄F, pH 6.0). The cell voltage was kept constant in the range from 10 to ~80 V for 120 min. Experimental condition are summarized in Table 3.

Table 3. Experimental conditions for the study of the effect of the cell voltage on TiO₂ films morphology.

Sample	Voltage (V)	H ₂ O (%)	EG (%)	NH ₄ F (%)	Time (min)
17	~80	5	95	0.250	120
9	70				
18	50				
19	30				
20	10				

9.5 Influence of synthesis time on TiO₂ film morphology

The electrolytic solutions contained 5% water + 95% ethylene glycol. The cell voltage was kept constant at 30 or 70 V and the reactions run in the time range from 10 to 120 min. Experimental condition are summarized in Table 4.

Table 4. Experimental conditions for the study of the effect of electrolysis time on the TiO₂ film morphology.

Sample	Voltage (V)	H ₂ O (%)	EG (%)	NH ₄ F (%)	Time (min)
21	70	5	95	0.250	10
22	70				30
23	70				60
9	70				120
24	30				10
25	30				30
26	30				60
19	30				120

9.6 Annealing temperature and crystallographic structure of TiO₂

Films prepared in 5% water + 95% ethylene glycol (0.25% NH₄F, pH 6.0) at 30 V for 120 min were annealed in a MTI GSL 1500X oven. The oven temperature was ramped from 25 °C at 4 °C/s up to an annealing temperature in the range from 300 to 700 °C and kept steady for 3 h. Then, a cooling ramp at 4 °C/s was applied. Diffractograms of the annealed samples (in the range of 20–100 °) were attained with an X-ray diffractometer (X'Pert³ MRD, PANalytical) with Cu K α radiation, 40 kV, and 40 mA. X'pert High-Score plus was used as analysis tool for phase identification. The experimental condition are summarized in Table 5.

Table 5. Experimental condition for the study of the effect of annealing temperature on crystallographic structure of TiO₂.

Sample	Voltage (V)	H ₂ O (%)	EG (%)	NH ₄ F (%)	Time (min)	Annealing Temperature (°C)
27	30	5	95	0.250	120	300
28						450
29						600
30						700

The morphological feature of TiO₂ nanostructure array films were determined with a field emission scanning electron microscope (FE-SEM; SUPRATM 40, Carl Zeiss) at 5.00 kV with magnifications from 2.00 KX to 400.00 KX at Universidad de Buenos Aires, Argentina by Dr. Claudia Marchi. The ImageJ software was used as analysis tool for nanotubes diameter and length. Top inner diameter of TiO₂ nanotube was measured assuming circular shapes. Then, the histogram of top inner diameter were fitted to Equation 1. Where x_c is the inner diameter and $\sigma = w/2$ is the standard deviation. The error bars in the figures represent \pm standard deviation.

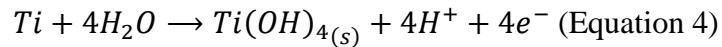
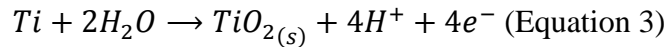
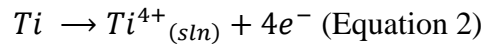
$$y = y_0 + \left(\frac{A}{w \sqrt{\frac{\pi}{2}}} \right) * e^{-2 \left(\frac{(x-x_c)}{w} \right)^2} \text{ Equation 1}$$

10. RESULTS AND DISCUSSION

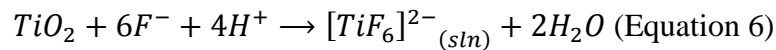
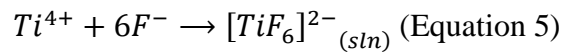
This section focuses on the set of experimental conditions for which well-organized nanostructures grow on the titanium anode surface. Formation of regular arrays of nanotubes is favored by electrolysis media that contain relatively high concentrations of fluoride ions in a mostly organic solvent with low concentration of water.

10.1 Morphology of TiO₂ films prepared in acidic medium as a function of electrolysis time

A first series of films was synthesized in an acidic medium at pH 2.1. Figure 3 shows micrographs of the external surface of TiO₂ films grown for 2, 5 and 10 h (images a, b, and c, respectively). The film shows deep craters with complex, cave like internal structure, very thin walls (of the order of 10 nm), and no apparent order regardless of the electrolysis time. In an aqueous environment, the anodic polarization of Ti involves the simultaneous formation of soluble species of Ti⁴⁺ and a thin layer of a mixed oxide-hydroxide layer Ti(O)_x Ti(OH)_y through reaction with water oxidation intermediates.



The presence of fluoride ions contribute to the formation of soluble [TiF₆]²⁻ through



The morphology of the electrochemically grown oxide layer depends on several competing processes. It has been shown that, in acidic electrolytes, chemical dissolution of the oxide layer is fast, hindering the formation of ordered nanostructures³.

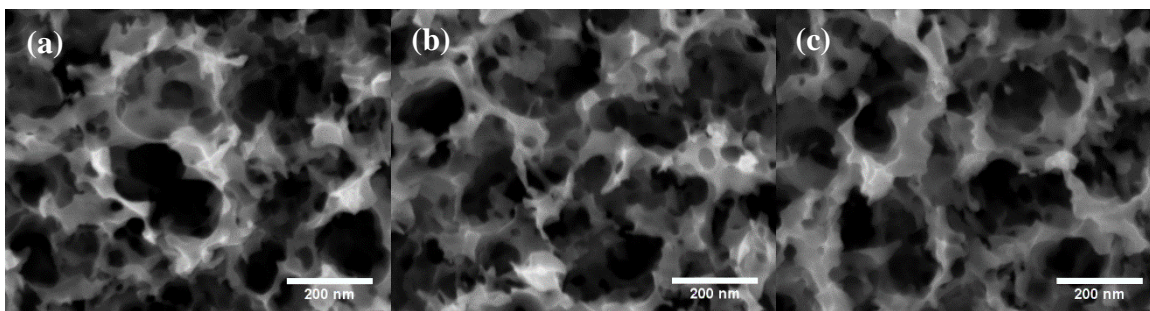


Figure 3. SEM images of TiO_2 films grown in 50% water + 50% ethylene glycol (containing 0.2% HF at pH 2.1) at 70 V for (a) 120, (b) 300, and (c) 600 min.

In the search for highly ordered films, other sets of experiments were performed in a more neutral medium by decreasing the water content and switching from HF to NH_4F , thus increasing the cell pH from 2.1 to 6.0.

10.2 Influence of fluoride ion concentration on TiO_2 films morphology

Figure 4 shows morphological features of TiO_2 films anodically grown on Ti in a mixed solution (5% water + 95% EG) containing (a) 0, (b) 0.15, (c, d) 0.45% NH_4F . In the absence of fluoride ions (a), the as-grown film is relatively compact with a flaky structure and cracks. In (b) some stratified substructures are visible. Increasing the NH_4F concentration to 0.45% (c + d) results in a film with an external side (the one in contact with the electrolysis solution) characterized by an irregular distribution of circular and oval pores with mouth diameter well below 100 nm. The side view reveals a film thickness of ~ 250 nm and some domes protruding from the internal side of the film (the one in contact with the titanium foil). In Figure 4 (d) shows the underlying Ti surface shows crater whose diameter are much larger than those of the pores at the external film surface.

Films with more regular morphology are observed by further increasing the concentration of NH_4F , Figure 5. Electrosynthesis in a 0.075% NH_4F -containing solution, yields films with a tubular structure (Figure 5a). Figure 5a shows the side and the bottom of the tubes. The film was lifted off from the titanium surface. The inset is a top view of the film and shows some irregular material growing on the mouth of the tubes which is a remnant of the initial barrier layer formed during the early stages of anodization. The ribs around the tubes are attributed to the presence of water in the electrolysis solution¹⁷. Comparison of the top view and the

bottom of some broken tubes shows that a thickness gradient develops along the tube main axis so the top of the tubes is thinner than the bottom. This feature is also observed in Figure 5b and c. Other studies have revealed that, while the top of the tubes is pure TiO_2 , the bottom is rich in fluoride and tends to accumulate carbon from the decomposition of the organic solvent³. The film grown in the 0.15% NH_4F medium, Figure 5b, exhibits a defined squared array of tubes, while that grown in 0.25% NH_4F , Figure 5c, exhibits squared and hexagonal arrays. A closer look at the inset in Figure 5c reveals that some windows have been opened at the inner walls, connecting the tubes. Figure 5d shows a film grown in 0.50% NH_4F . The inset, a top view of the film, shows interconnecting pores inside the tubes.

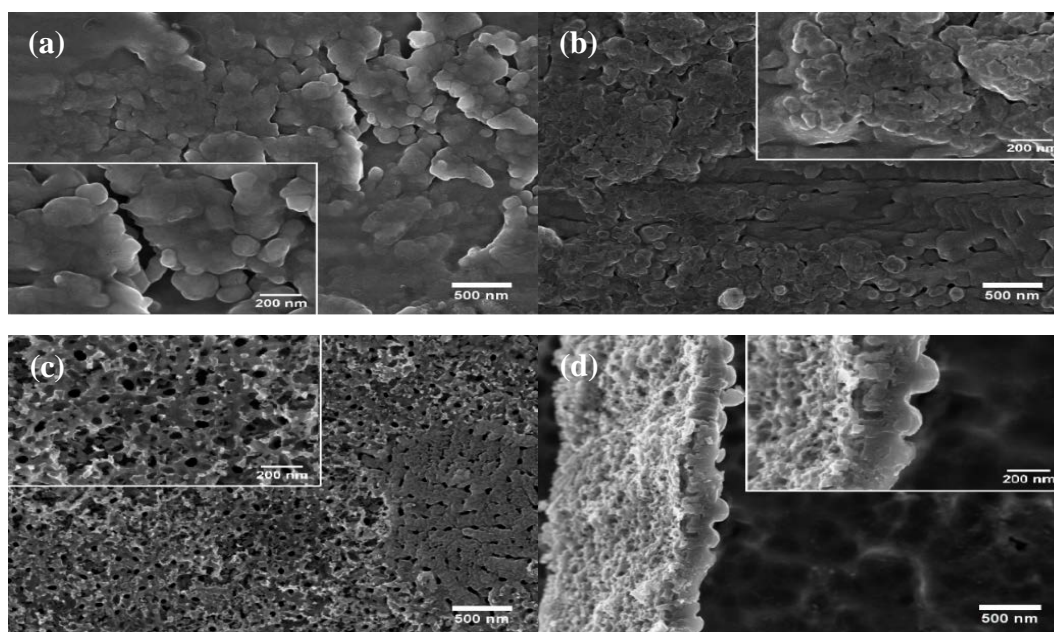


Figure 4. SEM images of TiO_2 films grown in 5% water + 95% ethylene glycol (containing NH_4F at pH 6.0) at 70 V for 120 min. The electrolysis medium contains (a) 0, (b) 0.015, and (c + d) 0.045% NH_4F . Image (d) is a cross-section view of (c).

In general, the chemical composition gradient along the tubes is most likely to be accompanied by a hydrophobicity gradient, that is, the tube internal surface would be more hydrophobic at the tube bottom than at the top, suggesting that, upon anodization, the composition of the electrolyte inside the pores changes with respect to that of the bulk electrolytic solution. Furthermore, it is also likely that a solvent composition gradient develops inside the pores.

The thickness of the film grown in the 0.075% NH_4F medium, Figure 5a is 6.5 μm while that of those films grown at higher NH_4F concentrations becomes constant at 9.4 μm . The top diameter of the tubes changes with NH_4F concentration in the range from 0.075 to 0.50% reaching a maximum of ca. 120 nm in the intermediate NH_4F concentrations. These facts are not well understood at this time (see Figure 6).

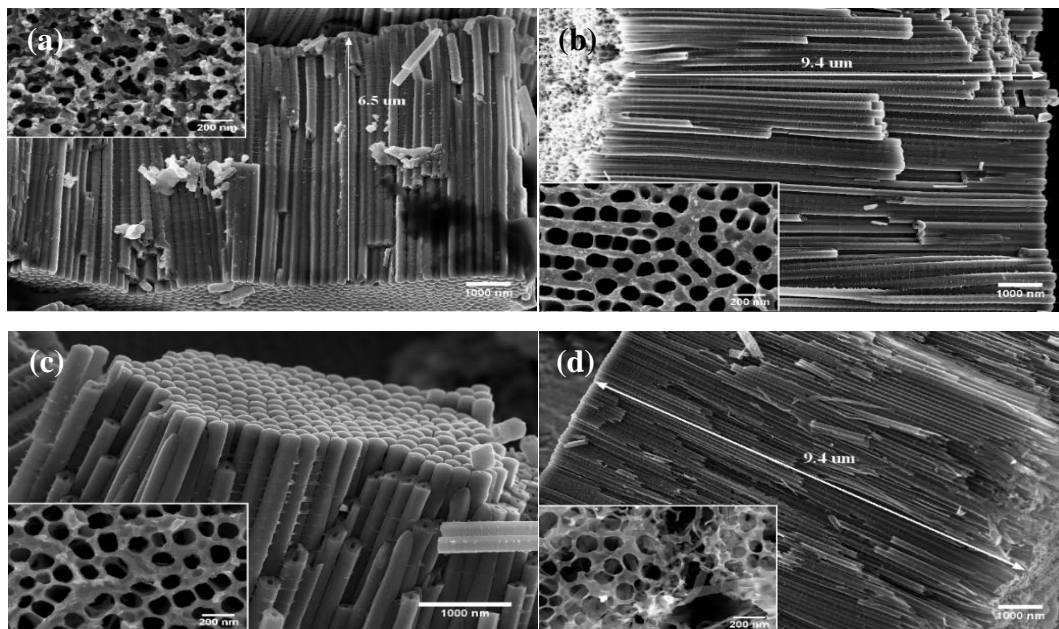


Figure 5. SEM images of TiO_2 films grown in 5% water + 95% ethylene glycol (containing NH_4F at pH 6.0) at 70 V for 120 min. The electrolysis medium contains (a) 0.075, (b) 0.15, (c) 0.25, and (d) 0.50% NH_4F .

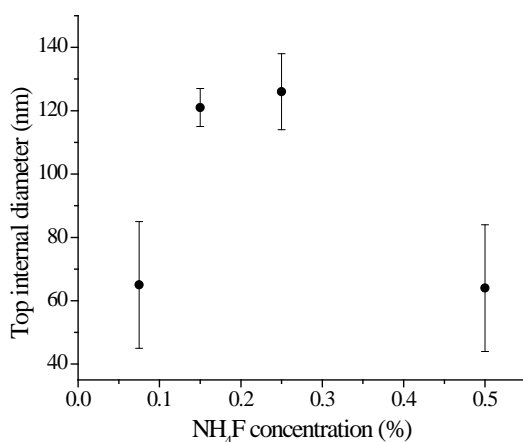


Figure 6. Top internal diameter of TiO_2 nanotubes as a function of fluoride content in the electrolyte solution. Anodization was carried out in 5% water + 95% ethylene glycol (containing NH_4F at pH 6.0) at 70 V for 120 min.

Figure 7 shows current density curves recorded during anodizing of Ti electrodes in 95% EG: 5% water containing different concentrations of NH_4F . In the absence of NH_4F , the current rapidly drops below the minimum current detected by the ammeter in the power source. For NH_4F concentrations in the range from 0.015 to 0.075%, the current drops continuously. For the curves with 0.045 and 0.075 % NH_4F , the curves become practically superimposable after a few minutes of electrolysis and the current drops with $t^{-1/2}$ indicating that the electron transfer at the Ti electrode becomes controlled by diffusion of electroactive species from the bulk solution. The fact that the current does not abruptly drop to zero indicates that the growing solid oxide layer does not passivate the titanium surface and allows for mass transfer and charge migration between the electrodes at the outside bulk solution. The current profile changes drastically as the NH_4F concentrations are moved to the range from 0.15 to 0.5%. Here, after a drop in the first minutes, the current rises, reaches a maximum and decays again. The current peak, which becomes sharper and occur shorter time with NH_4F concentration, indicates that the surface of the electrode is notoriously increasing.

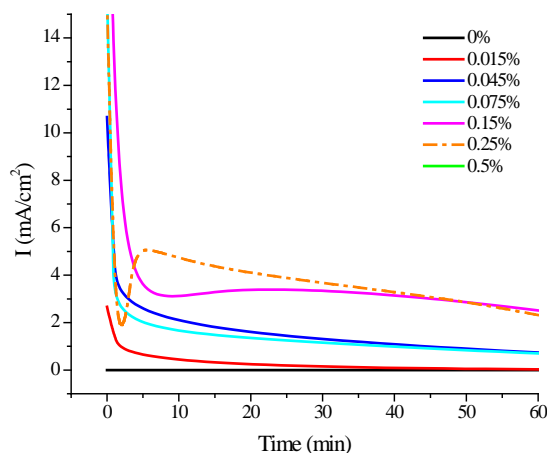


Figure 7. Current density profile upon anodization of titanium at 70 V in a cell containing 95% EG: 5% water containing ammonium fluoride. Color lines indicate concentration of NH_4F .

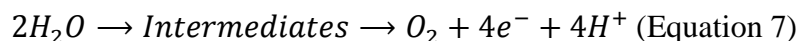
10.3 Influence of the water content on the morphology of TiO_2 films

This section shows the influence of the water content in the media (in the range from 0 to 10%) on film morphology. The concentration of NH_4F was kept constant at 0.250% NH_4F .

Figure 8 shows morphological features of TiO_2 films anodically grown on Ti in a solution containing approximately (a) 0, (b) 2, (c) 4, (d) 6, (e) 8, and (f) 10 water. Because ethylene

glycol was used as purchased, we cannot claim an exact percent of water. EG is hygroscopic and it may pick up water from the environment as the reaction proceeds. For better control of water content in the electrolysis solution, experiments would have to be carried out in a dry box.

Figure 8a shows images of a film prepared in a ~0% water medium. The structure is a distorted hexagonal array of pores. The bottom of some broken pores drilled in the oxide structure exhibit an inner diameter of ~40 nm with much thicker hexagonal cell boundaries. Electrolysis in solutions that contain at least 2% of the water percent yields films with a well-defined tubes with thinner walls and ribs around tubes^{1,14}. The ribs around the tubes have been attributed to the presence of oxygen that evolves during the oxidation of water, Equation 7¹⁴, although no plausible explanation of the mechanism of ring formation is available.



Films grown in water are characterized by distorted hexagonal arrays, except for the film grown in the ~6% water, Figure 8d, which exhibits squared and hexagonal arrays. The fact that the films have different array distribution are, perhaps, a consequence of the polycrystalline surface of the titanium foil. Studies on the growth of TiO₂ on single crystal Ti(111), and Ti(001) have shown that nanotube orientation depends on the metal surface crystal planes exposed to electron transfer and ion etching¹⁸.

Figure 9 shows the relationship between the fraction of the water content and the top internal diameter of TiO₂ nanotubes. Data dispersion is relatively high as indicated by the magnitude of the error bars, which represent \pm standard deviation.

However, the trend is for the tubes to become wider and thinner as the water content increases in agreement with the role of water as facilitator of oxide etching.

Interpretation of the curves Figure 10 is as in Figure 7. No apparent pattern for the evolution of the current is observed here. We hypothesize that difference in electrode pretreatment may seriously affect the current-time profiles. This is well known for the growing of other materials, such as conducting polymers, on electrodes.

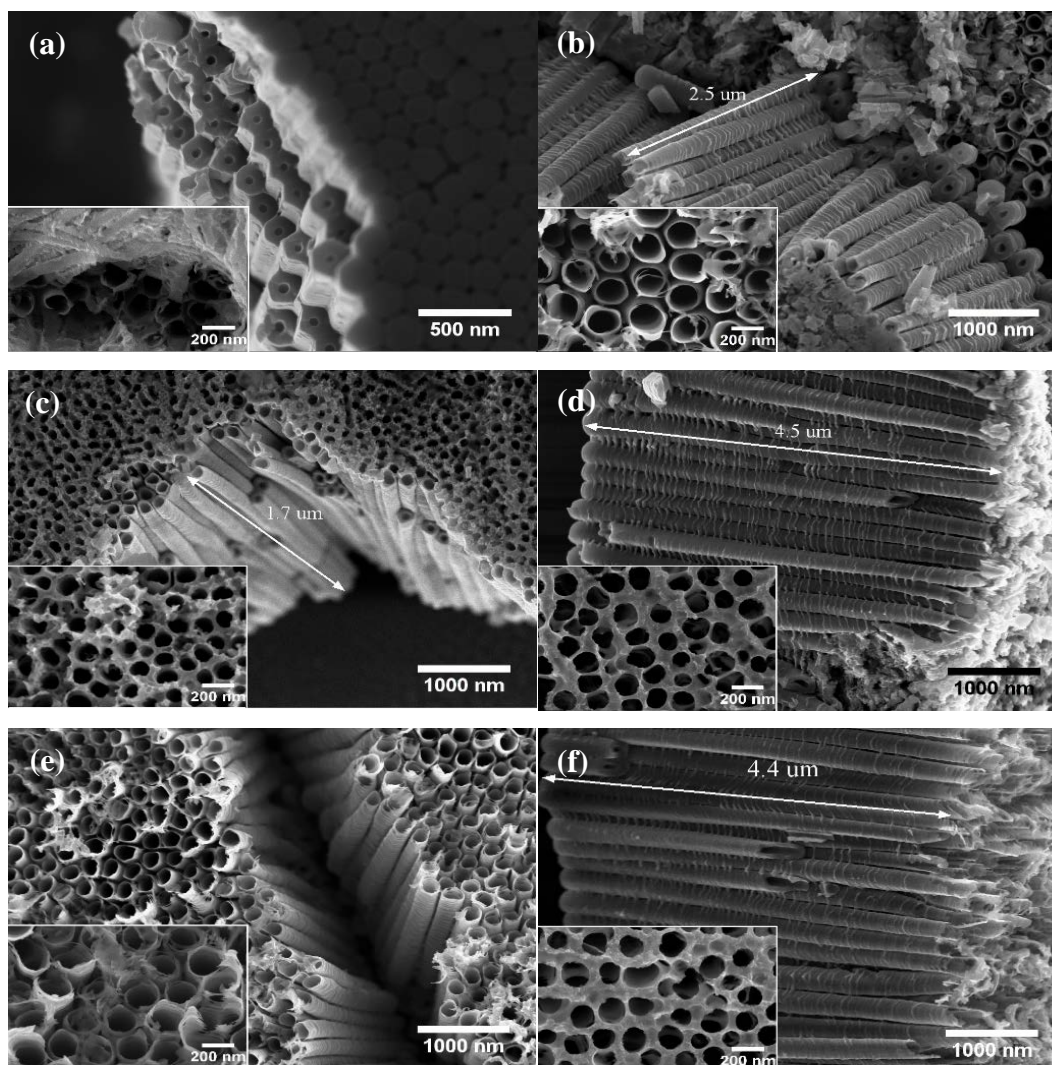


Figure 8. SEM images of TiO_2 films grown in water + ethylene glycol (containing 0.25% NH_4F at pH 6.0) at 70 V for 120 min. The approximate water concentration in the electrolysis medium is (a) 0, (b) 2, (c) 4, (d) 6, (e) 8, and (f) 10% H_2O .

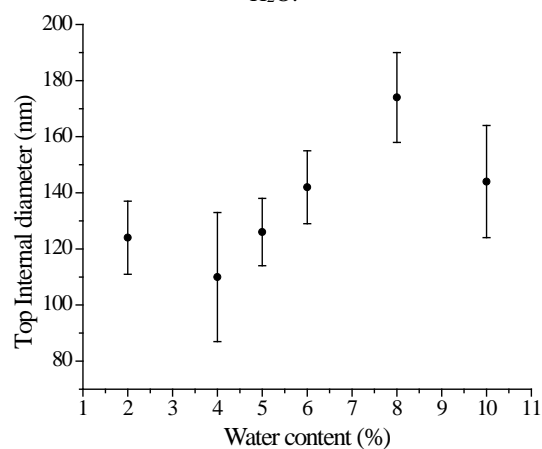


Figure 9. Top internal diameter of TiO_2 nanotubes as a function of water content in the electrolyte solution. Anodization was carried out in water + ethylene glycol (containing 0.25% NH_4F at pH 6.0) at 70 V for 120 min.

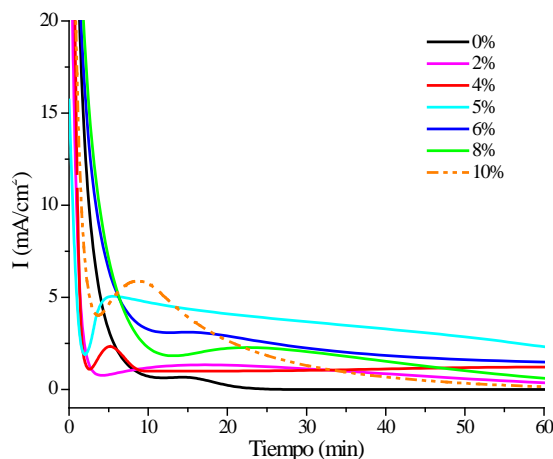


Figure 10. Current density profile upon anodization of titanium at 70 V in a cell containing 0.25% NH_4F in different EG: water containing at 70 V. Color lines indicate approximately water content.

10.4 Effect of the cell voltage on TiO_2 film morphology

In this series of experiments, the anodization of Ti was performed at constant cell voltage in the range from 10 to 80 V. Here, it is worth mentioning that this is the voltage across the cell, that is, between the cathode and the anode, not the potential difference between the anode and some reference electrode. In addition, not all of the applied cell voltage is used for electrochemical reactions (also called Faradaic processes) at the anode and the cathode. Some of the applied voltage is used to compensate for the electrolytic medium resistance. Without a reference electrode the exact applied potentials at the anode or cathode are unknown. For the experiment at 80 V, the power source could not hold the voltage. Thus, the current profile is not necessarily representative.

Figure 11 shows morphological features of TiO_2 films anodically grown on Ti in a 95% EG: 5% water content (containing 0.25% NH_4F) at 80, 50, 30, and 10 V (images a, b, c, and d, respectively). The micrograph of the TiO_2 film grown at 80 V, Figure 11a, shows bundles of nanotubes that spontaneously peeled from the titanium surface. The inset shows a sheet of oxide rings on top of the nanotubes. At 50 V, Figure 11b, the external surface exhibits a grassy structure, which is attributed to the partial dissolution of the nanotube wall¹⁴. The film grown at 30 V, Figure 11c, shows a distorted hexagonal distribution of tubes. This hexagonal arrays is more clearly seen on the underlying titanium film. At film grown at 10 V, Figure

11d shows no tubular structure.

Nanotube length increased with cell voltage. The film grown at 80 V, Figure 11a, is 24 μm -thick, while those grown at 50, and 30 V is 5.2 μm and 1.7 μm -thick, respectively.

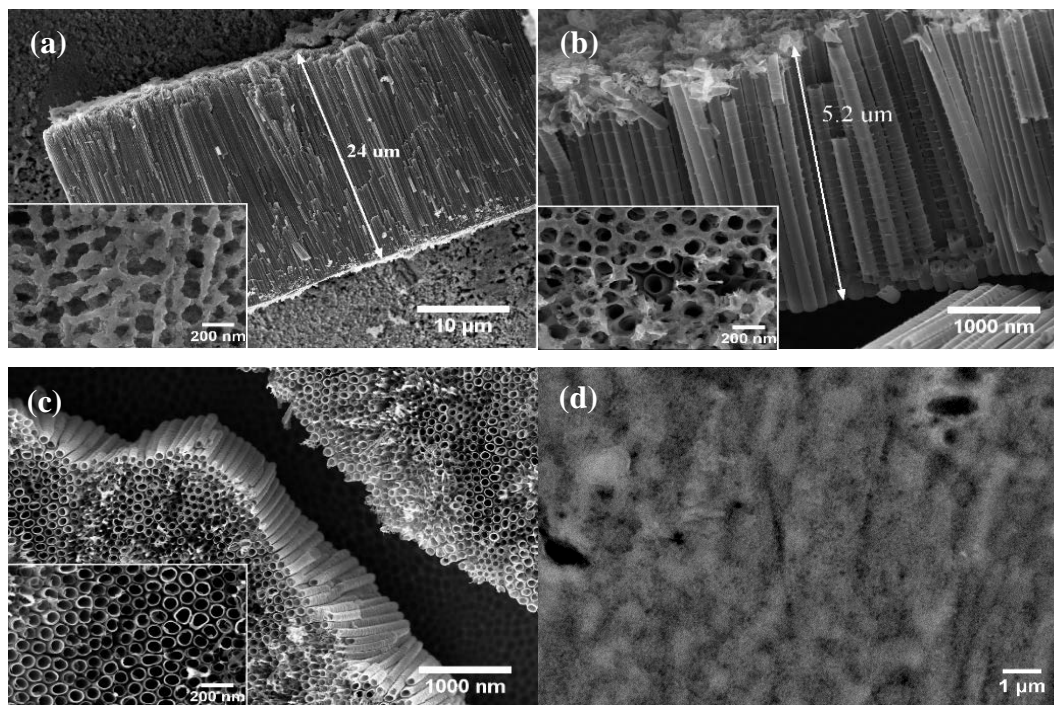


Figure 11. SEM images of TiO₂ films grown in ethylene 5% water + 95% ethylene glycol (0.25% NH₄F at pH 6.0) for 120 min. The anodization of Ti was performed at constant cell voltage: (a) 80, (b) 50, (c) 30, and (d) 10 V.

Several SEM images displayed above clearly show a non-uniform oxide layer on top of the nanotubes. But, depending on the electrosynthesis conditions and the film thickness, the appearance of this layer changes as shown in Figure 8 and 11. Elimination of this top layer to obtain well defined nanotubes is important for some applications, for instance, in separation processes. In this regard, the study of the factors that determine the morphology of this top layer are useful.

Figure 12 shows the relation between top internal diameters of the nanotubes the cell voltage. Apparently, in the range between 30 and 70 V, the film grow taller and the nanotube walls become thinner as the cell voltage increases, indicating that, under this set of conditions, formation of totally soluble titanium species does not yet limit the formation of solid oxide.

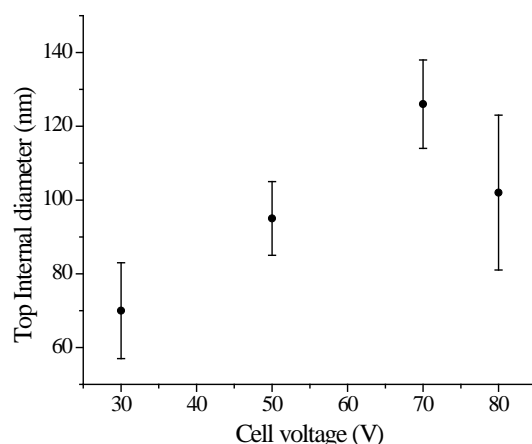


Figure 12. Top internal diameter of the TiO₂ nanotubes films as a function of cell voltage. The electrolysis medium is 5% water + 95% ethylene glycol (containing 0.25% NH₄F at pH 6.0) for 120 min.

10.5 Influence of synthesis time on TiO₂ film morphology

This set of experiments was performed in a cell containing 95% EG: 5% water content (containing 0.25% NH₄F) at 30 V and 70 V, conditions that allow for growth of regular nanotubes.

Figure 13 shows regular tubes structures of TiO₂ films anodically grown on Ti at 70 V for (a) 10, (b) 30, (c), 60, and (d) 120 min. Micrograph (a) shows regular tubular structures of TiO₂ are formed in the first 10 min of reaction. The tubes grown for 30 min are only 20% longer than the tubes grown for 10 min. For longer reaction times, the tube lengths do not increase any further in apparent contradiction to what others have previously reported.

Figure 14 shows current density curves recorded during the electrosynthesis of the films shown in Figure 13. Because reaction time was the only difference among these experiments, one might expect the curves for the shorter reaction times to be superimposable on the curves for longer reaction times. However, the current densities and profiles vary from one film to another. The lack of reproducibility of the current profiles could be related to the little variations in the electrode position in the cell, differences in the titanium surface pretreatment and changes in the time the electrodes were in contact with the electrolyte solution before electrolysis. Even differences in stirring rate from one experiment to another may contribute to changes in the current profiles. Notice that, although the films grown for 30 min and up

are thicker than the one grown for 10 min, it is precisely the film grown for 10 min that shows the highest current profile. If most of the electric charge passed during electrolysis were used to build the film, one would expect at least a rough correlation between charge passed upon electrolysis (calculated by integration of the I-t curves) and film thickness. For the 10, 30, and 120 min reactions, one gets 7.88, 21.7, and 18.2 C, respectively. On the other hand, the corresponding film thicknesses are 6.5, 7.8, and 8.0 μm . Increasing the reaction time from 10 to 30 min produces an almost linear increase in charge.

However, in this same time span, the film thickness increases merely by about 20%. The difference between the charge/rxn time and film thickness/rxn time ratios suggests that a higher percentage of titanium is solubilized during the 30 min electrolysis. As a result, the tubes in the 30 min film should be thicker, and, presumably, their walls should be thinner than those of the 10 min film. However, when the reaction time increases from 30 to 120 min, the charge actually decreases a little, which defies explanation is not limited by titanium oxidation (independently of whether titanium oxidation leads to soluble species or to oxide formation).

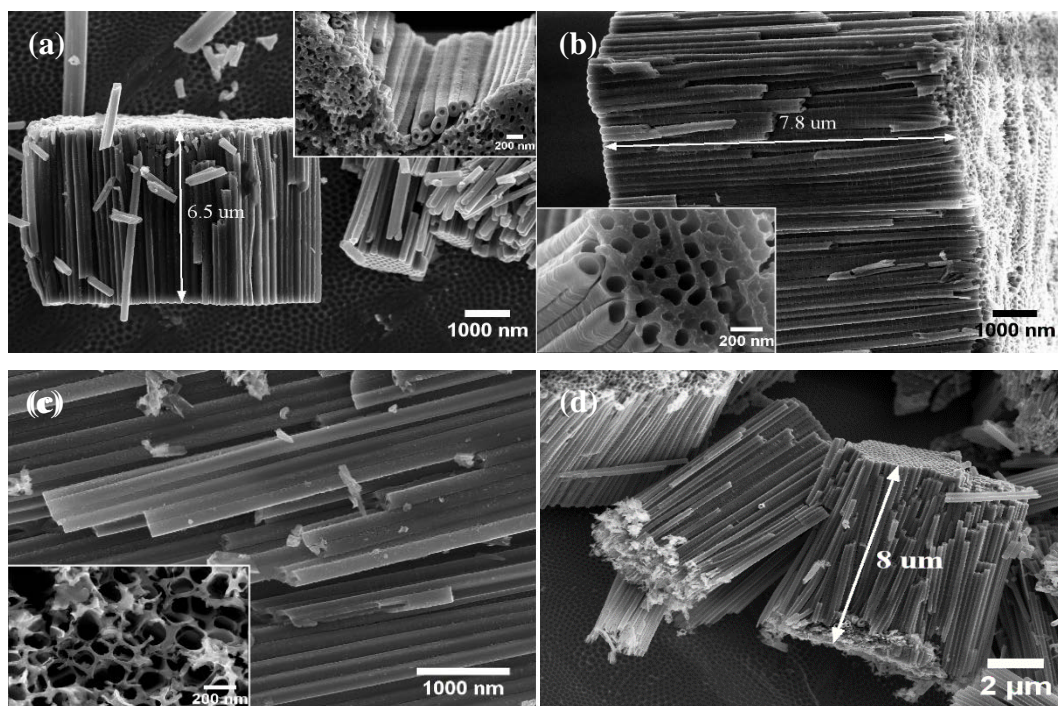


Figure 13. SEM images of TiO_2 grown in 5% water + 95% ethylene glycol (containing 0.25% NH_4F) at 70 V. Electrolysis time is (a) 10, (b) 30, (c) 60, and (d) 120 min.

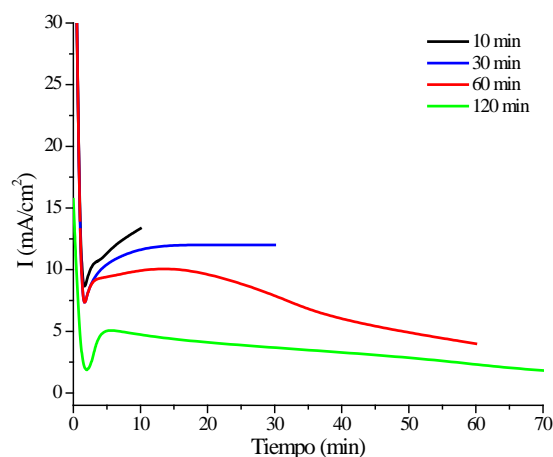


Figure 14. Current density-time curves acquired upon anodization of Ti in 5% water + 95% ethylene glycol (containing 0.25 % NH_4F) at 70 V. Color lines indicate electrolysis time.

Figure 15 shows regular tubes structures of TiO_2 films anodically grown on Ti at 30 V for (a) 10, (b) 30, and (c), 60 min. The most striking feature is that, in the 10 to 60 min reaction time window, the films grow almost linearly with time, unlike the films at 70 V. In perspective, it means that at 30 V the electrolysis rate is limited by oxide formation while at 70 V it is not.

Figure 16 shows plots of current density vs electrolysis time for the films grown at 30 V. In this case, calculation of the area under the I-t curves gives 2.36, 3.08, 2.20, and 2.27 C, for the 10, 30, 60, and 120 min reactions, respectively. Thus, with one apparent exception, the anodic charge is almost independent of electrolysis time although the film thickness was shown to steadily increase with reaction time.

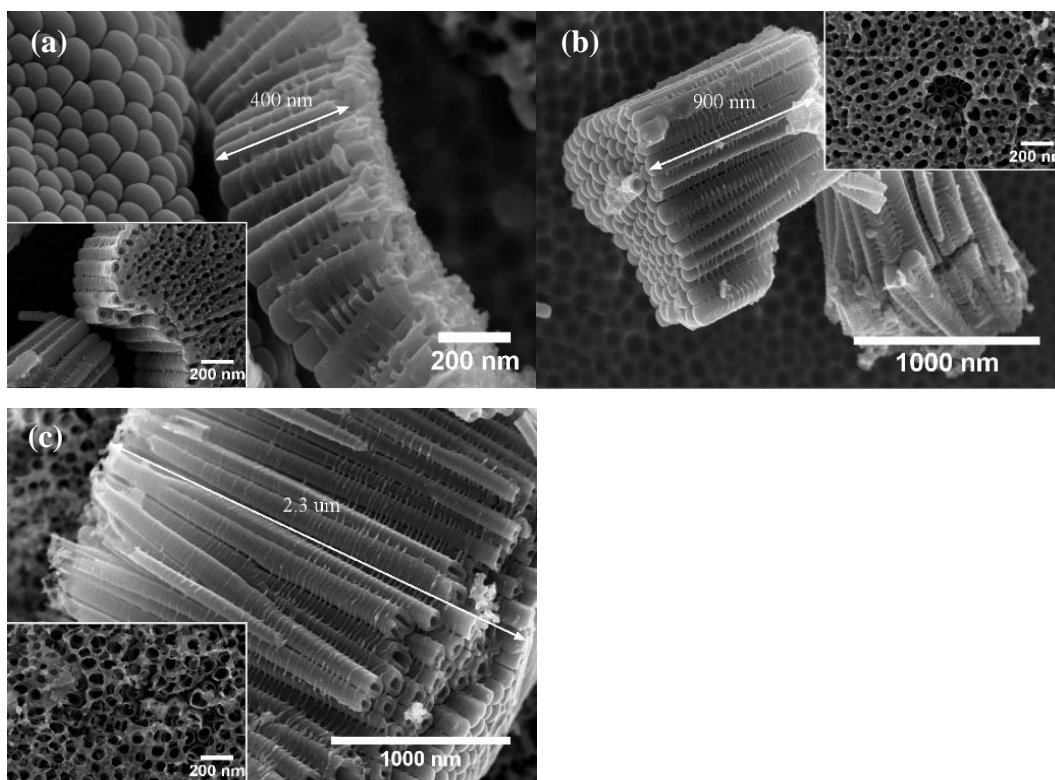


Figure 15. SEM images of TiO_2 grown in 5% water + 95% ethylene glycol (containing 0.25% NH_4F) at 30 V. Electrolysis time is (a) 10, (b) 30, and (c) 60 min.

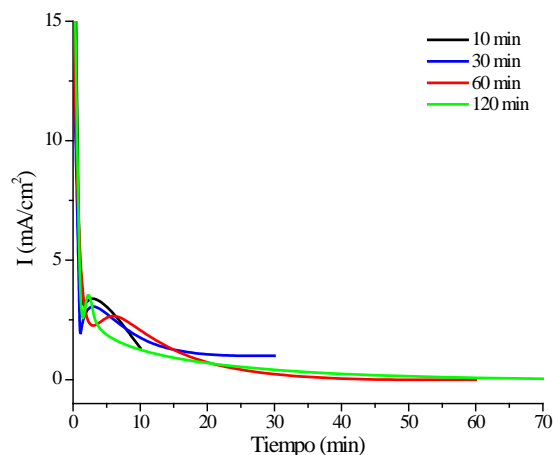


Figure 16. (a) Current density-time curves acquired upon anodization of Ti in 5% water + 95% ethylene glycol (containing 0.25 % NH_4F) at 30 V. Color lines indicate electrolysis time.

The purpose of this exploratory work was to produce arrays of TiO_2 nanotubes and elucidate the influence of the most evident experimental factors on the nanotubes length and thickness because fine control of these two feature determines the application of the resulting films. There is an ongoing discussion regarding the mechanism or mechanisms that lead to the self-assembly of nanotubes and all of the discussions assume that only the anodic reactions and

their coupled chemical reaction play a role. However, at least two factors may have been overlooked. The first is the nature of the fluorine species that participate in the formation of the oxide and somehow orient the growth of nanotubes. Given the high cell voltages used for the synthesis of TiO₂ and the fact that both water and the organic solvent are decomposed at the anode, the formation of species containing oxygen and fluorine may play a role in the electrosynthesis of the oxide films. The second factor is the set of conditions under which the reaction or reactions at the cathode may limit the overall process in the cell. It is a known fact in electrochemical synthesis that the area of the counter electrode (the cathode, in our case) must be much higher than that of the “working electrode” (the anode in our case). In this work, the cathode was a platinum foil of geometric area $\approx 1\text{cm}^2$, that is, before the electrolysis begins, the area of the cathode is twice of the anode. However, the I-t curve clearly show that the area of the anode increases upon electrolysis. Depending on the conditions, the rate of the overall process at the cell might become limited by the reactions at the cathode. In additions, it would be important to clearly determine whether species produced at the cathode diffuse to interact with species near the anode.

10.6 Annealing temperature and crystallographic structure of TiO₂

Sample 30 at 30 V for 120 min (see Table 5) were annealed at 300, 450, 600, and 700 °C in air for 3 h after a heating ramp from 25 °C to the set temperature (4 °C/s). After annealing, the samples were cooled to room temperature at 4 °C/s. Figure 17 shows XRD patterns of TiO₂ at different annealing temperatures.

The diffractogram of a control, shows peaks for titanium only. The diffraction peaks at 35, 38, 53, 70, and 76 ° correspond to the (010), (002), (012), (013), and (112) Ti crystal planes, respectively. As expected, the anodically grown films are amorphous.

Peaks ascribed to the anatase phase are visible for all of the annealed films. As expected, peaks for the rutile phase are observed in the diffractograms of the sample annealed at 600 and 700 °C, which contain 20 and 94% rutile, respectively.

The signals related to titanium are highly attenuated upon annealing to give way to the uprising of the rutile related peaks, these features have been attributed to the transition to rutile takes place at the Ti/TiO₂ interface¹⁴.

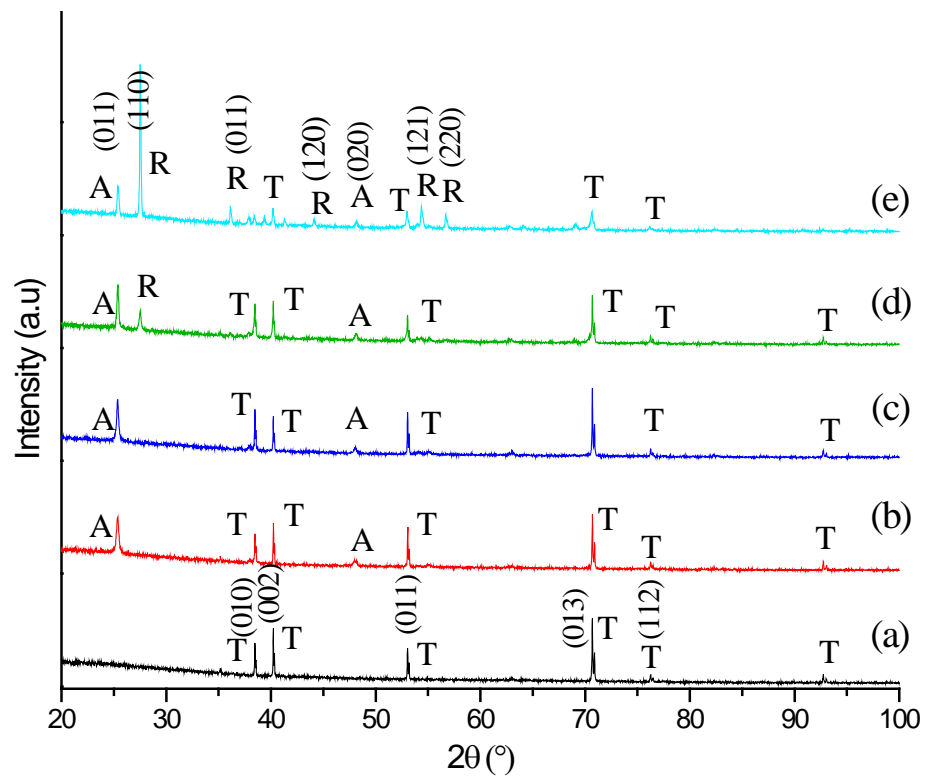


Figure 17. XRD of TiO₂ annealed at (b) 300, (c) 450, (d) 600, and (e) 700 °C. Diffractogram (a) is a control experiment: (film grown at 25 °C).

11. CONCLUSIONS

Electrosynthesis of TiO_2 in ethylene glycol + aqueous electrolysis media (containing either HF or NH_4F) lead to the formation of films with morphologies that are very dependent on solvent composition and total fluoride concentration.

The formation of self-organized nanotube structures is favored in mostly organic solutions and the morphology of the nanotubes is strongly dependent on fluoride ion concentration. Most of the nanotube films are characterized by a more compact oxide layer on top and by very symmetrical ribs on the tube side wall. Although the overall shape of the I-t curves recorded during electrolysis can be used to assess the formation of oxide films with high surface, the reproducibility of these curves is very poor suggesting that unaccounted factors heavily influence electron transfer at the Ti/solution or Ti/oxide interfaces.

For the films grown at 30 V, the nanotube arrays and the underlying Ti surface show hexagonal patterns, indicating the highly correlated drilling of the surface, difficult to explain if one considers that the titanium foils used here are polycrystalline.

The electrochemically grown films are not crystalline but transition to the anatase and rutile phases are observed upon annealing of the films in the range between 300 and 600 °C.

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